LEACHING OF ORGANIC RESIDUALS FROM SIMULATED IN SITU RETORTED OIL SHALE

G. L. Amy,[1] J. F. Thomas,[1] and A. L. Hines[2]

[1]Sanitary Engineering, University of California, Berkeley, CA 94720
[2]Chemical and Petroleum-Refining Engineering,
Colorado School of Mines, Golden, CO 80401

Introduction

Various economic and environmental constraints have thus far inhibited development of oil shale resources by surface-retorting technologies. In an attempt to overcome these constraints, recent attention has focused on in situ methods of retorting oil shale.

In certain geographical areas, oil shale occurs as a continuous, relatively impermeable layer situated between two groundwater aquifers. An example of this situation is the Piceance Basin in Colorado where a rich layer of oil shale known as the Mahogany Zone persists throughout most of the basin. In areas such as the Piceance Basin, a major environmental hazard associated with in situ development is that it may potentially contaminate groundwater from adjacent aquifers. This potential contamination may evolve as a consequence of various organic and inorganic species being leached from the spent shale by groundwater migration into an abandoned underground retort (1),(2). During retorting, oil shale is transformed from a relatively inert substance into an unstable material containing various water soluble organic and inorganic components. The purpose of this paper is to assess the potential for contamination of groundwater by various organic residuals leached from in situ type spent shale.

Leaching Experiments

Two types of laboratory experiments were conducted to assess the potential for contamination of groundwater by organic leachants. These included (1) preliminary batch experiments and (2) equilibrium batch experiments. Both of these leaching experiments examined a series of unique spent shale samples under various experimental conditions. The analytical parameter selected for monitoring the quality of leachate was Total Organic Carbon (TOC).

Spent Shale Samples

Spent shale samples examined during this study were obtained from Lawrence Livermore Laboratory's (LLL) pilot-scale 125-Kg simulated in situ retort. The raw oil shale used by LLL was mined from the Anvil Points area in Colorado. The Fischer Assay of the raw oil shale was 24 gallons per ton while the organic carbon content of the raw oil shale was 10.8% by weight.

The retorting conditions employed during the production of spent shale are summarized in Table 1. As shown in Table 1, these samples represent a wide cross-section of the types of spent shale that may be produced under various retorting conditions.

The physical characteristics (i.e., particle size range, density, and porosity) of the spent shale samples examined in the leaching experiments were generally similar. However, a major difference observed was their solid-phase organic carbon content. The solid-phase organic carbon content of Types 1, 2, 3, and 4 spent shales was 0.2%, 1.8%, 2.1%, and 3.9% by weight, respectively.

As anticipated, the Type 1 spent shale contained the least organic carbon since it was produced during combustion retorting. In contrast, the Types 2 and 4 spent

shales contained higher levels of organic carbon as a result of retorting in an inert gas atmosphere. The Type 3 spent shale is perhaps the most interesting with respect to organic carbon content. Since the Type 3 spent shale was produced during combustion retorting, it was initially anticipated that very little residual organic material would remain on the shale matrix. However, for this particular type of spent shale, it is important to note that recycle gas was employed as part of the input gas. Since recycle gas contains significant amounts of volatile organics (3), it is hypothesized that the high organic carbon content of the Type 3 spent shale may be due to either the adsorption of certain volatile organics originally present in recycle gas or the condensation of hydrocarbons onto the shale behind the flame front.

Table 1. Retorting Conditions Employed in Production of Spent Shale Samples.

	Spent Shale Samples			
Retorting Parameter	Type 1	Type 2	Type 3	Type 4
Type of Retorting Run	Combustion	Inert Gas	Combustion	Inert Gas
Input Gas	Air + N_2 (7.6% O_2)	N_2	Air + Recycle Gas (10.5% O_2)	N_2
Maximum Retorting Temperature (^oC)	750	510	935	-
Retorting Rate (meters/day)	0.69	1.40	1.34	-

Source; W. Sandholtz, Lawrence Livermore Laboratory, letters dated 11/4/76 and 12/20/76.

Preliminary Batch Experiments

The preliminary batch experiments consisted of placing a small mass of spent shale (50 grams) and a small volume of water (50 milliliters) into a series of flasks. After sealing, each flask was allowed to quiescently sit for a designated time period, ranging up to 30 days. At the end of the designated time period, the leachate was decanted, filtered, and analyzed for Total Organic Carbon (TOC). For each type of spent shale examined, leachate samples from a series of these flasks were allowed to sit for time periods ranging from 0.5 to 30 days and were subsequently analyzed for TOC. In most cases, "pseude-equilibrium" conditions were attained after 30 days of leaching.

The major impetus behind the preliminary batch experiments was to identify factors that influence the leaching of organic material. Several experimental variables were examined, including: (1) retorting conditions, (2) temperature of the leach water, and (3) the initial quality of leach water.

The two water temperatures examined were 20^oC and 80^oC. The lower of these temperatures, 20^oC, represents the room temperature of the laboratory in which the experiments were conducted and is considered to be approximately representative of ambient groundwater temperature. The higher temperature, 80^oC, is considered to be approximately representative of anticipated water temperatures within an abandoned retort which has not cooled. Groundwater migrating into an abandoned retort may initially be converted to steam which will condense at temperatures slightly less than 100^oC.

The two general categories of leach water examined were distilled water and synthetic groundwater. The distilled water was considered to be approximately representative of good quality groundwater. The synthetic groundwater was produced in the laboratory by adding specified amounts of $NaHCO_3$, Na_2CO_3, NaCl, and Na_2SO_4 to distilled water. The specific conductivity of the synthetic groundwater was 12,000 μmhos/cm and its pH was 9.0. The synthetic groundwater was considered to be approximately representative of groundwater found in the lower aquifer of the Piceance Basin; groundwater from this aquifer is characterized by high levels of sodium and the carbonates.

The results of the preliminary batch experiments conducted for a leaching time period of thirty days are summarized in Table 2. As shown, retorting conditions, water temperature, and initial quality of leach water significantly influenced the leaching of organic material.

Employing distilled water at a temperature of 20°C, the highest level of organic carbon was observed in leachate derived from the Type 3 spent shale. It is hypothesized that most of the water soluble organic compounds associated with the Type 3 spent shale were originally components of recycle gas that adsorbed onto the spent shale matrix. These were held by weak physical forces and were readily leachable. The lowest organic carbon level was detected in leachate derived from the Type 1 spent shale. This may be attributed to its low solid-phase organic carbon content. The levels of organic carbon in leachate derived from spent shale samples produced during inert gas retorting were intermediate to values found in leachate derived from Types 1 and 3 spent shales.

Table 2. Preliminary Batch Experiments

	Total organic carbon (TOC) leached, mg/100 g of spent shale			
Experiment type	Type 1	Type 2	Type 3	Type 4
30-day distilled water batch exps. @ 20°C	1.1	1.9	3.5	1.7
30-day distilled water batch exps. @ 80°C	1.3	3.1	2.9	3.1
30-day groundwater batch exps. @ 20°C	1.0	2.3	3.8	2.0
30-day groundwater batch exps. @ 80°C	1.0	5.8	3.4	4.7

Employing distilled water at a temperature of 80°C, the highest levels of organic carbon were observed in the leachate obtained from samples produced during inert gas retorting. A comparison of experiments conducted with distilled water at temperatures of 20°C and 80°C reveals that the leaching of organic material from Types 2 and 4 spent shales was significantly enhanced at the higher temperature. This was attributed to the increased solubility of organic compounds at the higher water temperature. An elevated temperature appeared to have little overall effect on the leaching of organic material from Types 1 and 3 spent shales.

Employing groundwater at 20°C, the highest level of organic carbon was detected in leachate derived from the Type 3 spent shale while the lowest level was detected in leachate derived from the Type 1 spent shale. The results of the groundwater experiments conducted at 20°C were generally similar to the results of the corresponding

distilled water experiments. This implies that, at 20°C, the initial quality of leach water had little overall effect on the leaching of organic material.

Using groundwater at 80°C, higher levels of organic carbon were found in the leachate obtained from spent shale produced by inert gas retorting than in other samples. A comparison of groundwater experiments conducted at 20°C and 80°C reveals that a higher temperature significantly enhanced the leaching of organic material from Types 2 and 4 spent shales. The above observations are similar to those made when using distilled water. For Types 2 and 4 spent shales, significantly greater quantities of organic carbon were found in leachates obtained when using groundwater at 80°C than in the distilled water experiments conducted at the same temperature. This implies that some kind of synergistic mechanism, involving both water temperature and initial quality, resulted in more organic material being leached from Types 2 and 4 spent shales during the high-temperature groundwater experiments than during the high-temperature distilled water experiments.

Equilibrium Batch Experiments

The equilibrium batch experiments consisted of placing a small mass of spent shale (50 grams) and a variable volume of water, ranging from 30 to 200 milliliters, into a series of flasks. Each flask was sealed and allowed to quiescently sit for a period of 30 days. After this period, the leachate was decanted, filtered, and analyzed for TOC.

The major impetus behind the equilibrium batch experiments was to generate data enabling the development of equilibrium isotherms. The results of the preliminary batch experiments suggested that 30 days was, in most cases, an adequate time period for the establishment of "psuedo-equilibrium" conditions. Consequently, a leaching time of 30 days was used.

The experimental variables examined during the equilibrium batch experiments were identical to those considered during the preliminary batch studies with the following exceptions: (1) only Types 1 and 2 spent shales were used and (2) a series of shale to water ratios were evaluated.

The results derived from the equilibrium batch experiments are presented in Table 3. As shown, the concentration of organic carbon in all leachates increased for greater shale to water ratios.

An attempt was made to model the data derived from the equilibrium batch experiments by employing both the Freundlich and Langmuir equations. The Freundlich model is defined by;

$$q = KC^{1/n} \quad (1)$$

where q = mass of solute adsorbed per unit mass of adsorbant
C = equilibrium concentration of solute
K & n = constants

Transforming the above equation into logarithmic form yields;

$$\log q = \log K + 1/n \log C \quad (2)$$

In contrast to the Freundlich model, the Langmuir equation is defined by;

$$q = \frac{abC}{1 + aC} \quad (3)$$

where a & b = constants

The Langmuir equation is often expressed in linear form as;

$$\frac{1}{q} = \frac{1}{b} + \frac{1}{ab}\,\frac{1}{C} \quad (4)$$

Table 3. Equilibrium Batch Experiments

Concentration of Organic Carbon (mg/l)

Type of Experiment	Type 1				Type 2			
	50 g + 30ml	50 g + 50ml	50 g + 100ml	50 g + 200ml	50 g + 30ml	50 g + 50ml	50 g + 100ml	50 g + 200ml
Distilled Water at 20°C	18	11	5.0	3.9	25	19	11	5.4
Distilled Water at 80°C	16	13	6.9	4.9	36	31	24	15
Groundwater at 20°C	19	10	6.9	3.6	25	23	10	6.7
Groundwater at 80°C	16	10	7.7	4.4	67	58	38	17

Mass Leached Per Unit Mass (mg/100 g)

	Type 1				Type 2			
	50 g + 30ml	50 g + 50ml	50 g + 100ml	50 g + 200ml	50 g + 30ml	50 g + 50ml	50 g + 100ml	50 g + 200ml
Distilled Water at 20°C	1.1	1.1	1.0	1.6	1.5	1.9	2.2	2.2
Distilled Water at 80°C	1.0	1.3	1.4	2.0	2.2	3.1	4.8	6.0
Groundwater at 20°C	1.1	1.0	1.4	1.4	1.5	2.3	2.0	2.7
Groundwater at 80°C	1.0	1.0	1.5	1.8	4.0	5.8	7.6	6.8

The Freundlich and Langmuir models were originally developed to describe the adsorption phenomenon. In some cases, experimental data will fit one model better than the other. If experimental data conform to the Freundlich model then a plot of log q versus log C should be linear. Correspondingly, if experimental data conform to the Langmuir model, then a plot of 1/q versus 1/C should be linear.

In order to apply the above adsorption models to a leaching/desorption phenomenon, it is necessary to redefine the parameters C and q. The parameter C is defined as the equilibrium TOC contration in the leachate, expressed in terms of mg/l. The parameter q is defined as the mass of organic carbon remaining on the spent shale per unit mass of spent shale (expressed in terms of mg TOC/g spent shale). The parameter q can be estimated by subtracting the mass of organic carbon leached, as defined by measurements of C, from the initial solid-phase organic carbon content of the spent shale sample.

A least squares computer subroutine was used to estimate constants for both the Freundlich and Langmuir models. Estimates of constants for each equation are presented in Table 4. Employing these constants, either model can be used to predict the equilibrium TOC concentration resulting from a particular shale to water ratio.

Table 4. Constants for Freundlich and Langmuir Models.

	Type 1 Spent Shale				Type 2 Spent Shale			
	Freundlich		Langmuir		Freundlich		Langmuir	
	K	n	a	b	K	n	a	b
Distilled Water at 20°C	1.98032	615.433	81.1577	1.99075	17.9688	3850.47	433.849	17.9846
Distilled Water at 80°C	1.97197	318.766	36.4383	1.99237	17.8187	408.520	19.1234	17.9995
Groundwater at 20°C	1.98256	816.308	111.354	1.99027	17.9638	3116.45	241.323	17.9852
Groundwater at 80°C	1.97152	274.904	36.5797	1.99405	17.7054	298.471	6.18471	17.9989

All data derived from the equilibrium batch experiments were plotted as log q versus log C and 1/q versus 1/C. The purpose of this graphical exercise was to examine the plots for linearity and thus, to ascertain whether a particular model was appropriate for various groups of data.

Experimental data obtained from the Type 2 spent shale are plotted according to the logarithmic form of the Freundlich Model in Figures 1 and 2 and according to the linear form of the Langmuir Model in Figures 3 and 4. Both the Freundlich and Langmuir equations appear to be fairly appropriate for modelling experimental data for the Type 2 spent shale.

In contrast to the Type 2 spent shale, the Freundlich and Langmuir equations appear to be less appropriate for modelling experimental data derived from the Type 1 spent shale. Although plots of log q versus log C and 1/q versus 1/C appeared to roughly follow a linear trend, they were not as linear as corresponding plots for the Type 2 spent shale. It appears that another isotherm model may be more appropriate.

Conclusions

Based on the results of the preliminary batch experiments, it is apparent that there exists a significant potential for contamination of groundwater by organic residuals leached from in situ spent shale, particularly spent shale produced during inert gas retorting or combustion retorting employing recycle gas. This contamination may preclude certain beneficial uses of groundwater in the immediate vicinity of abandoned in situ retorts.

Both the Freundlich and Langmuir equations appear to be fairly appropriate for modelling the leaching of organic material from spent shale samples produced during inert gas retorting.

Acknowledgements

The research described in this paper was jointly sponsored by ERDA and the Department of the Interior. Sincere appreciation is given to Lawrence Livermore Laboratory, in particular W. Sandholtz, for supplying samples of spent shale.

References

(1) G. Amy and J. Thomas, "Factors that Influence the Leaching of Organic Material from In Situ Spent Shale", Proceedings of Second Pacific Chemical Engineering Congress, 1977.

(2) H.W. Parker, "Simulated Groundwater Leaching of In Situ Retorted or Burned Oil Shale", 1976 (Quarterly Progress Report for Grant #G0254011 funded by ERDA for Texas Tech University.)

(3) Engineering Science, Inc., "Air Quality Assessment of the Oil Shale Development Program in the Piceance Creek Basin", 1974.

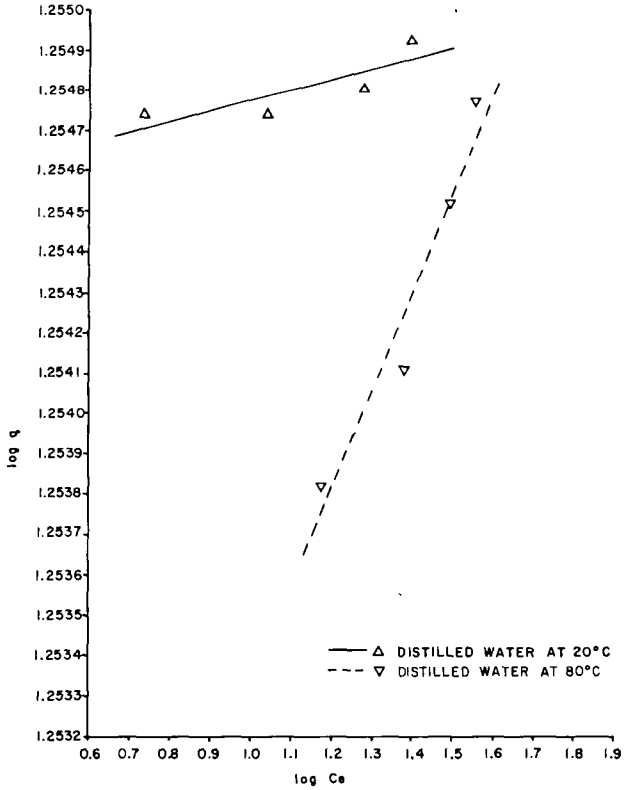

FIGURE 1. LOGARITHMIC FORM OF FREUNDLICH ISOTHERM FOR TYPE 2 SPENT SHALE/ DISTILLED WATER.

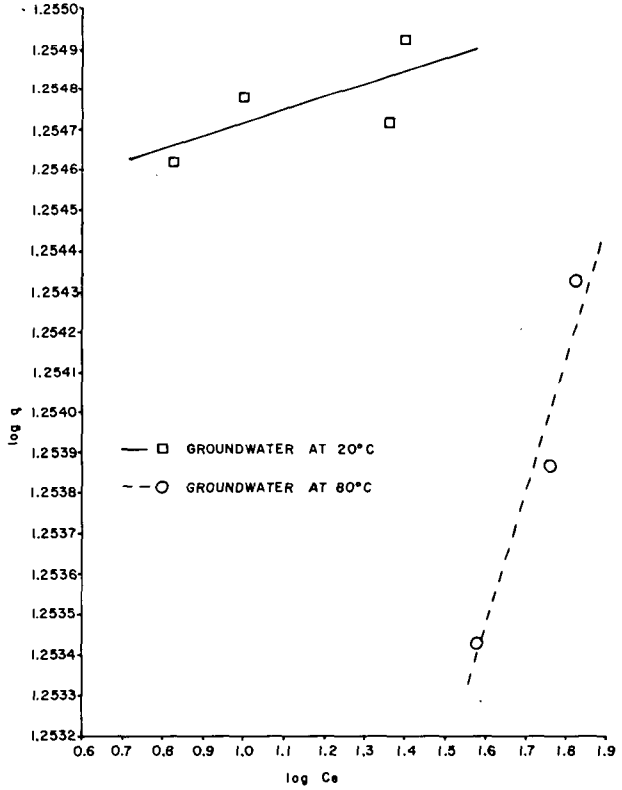

FIGURE 2. LOGARITHMIC FORM OF FREUNDLICH ISOTHERM FOR TYPE 2 SPENT SHALE/ GROUNDWATER.

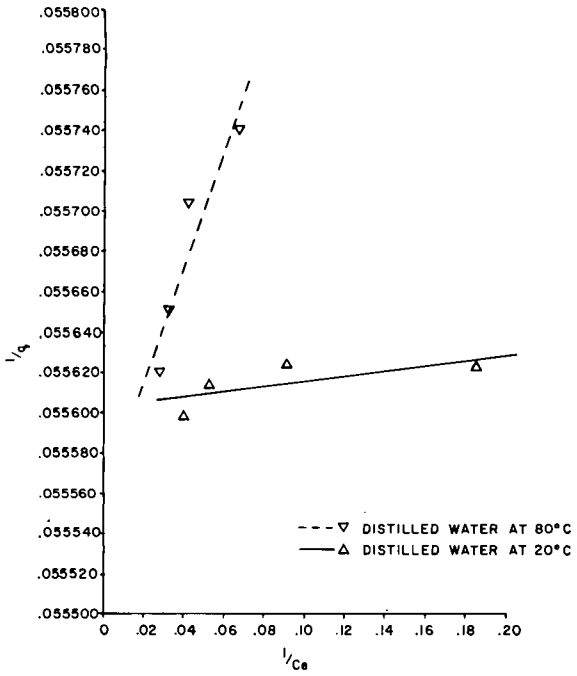

FIGURE 3. LINEAR FORM OF LANGMUIR ISOTHERM FOR TYPE 2 SPENT SHALE/DISTILLED WATER.

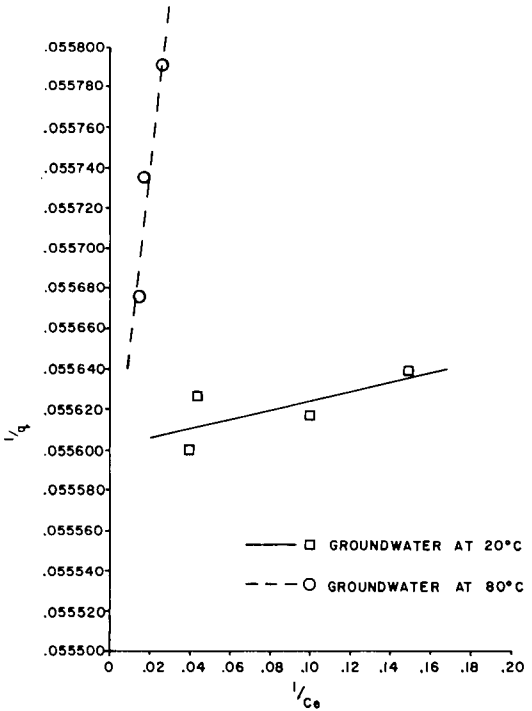

FIGURE 4. LINEAR FORM OF LANGMUIR ISOTHERM FOR TYPE 2 SPENT SHALE/GROUNDWATER.